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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification ⁵ : C08K 3/20, C08J 5/00, 5/10, C08L 59/02, 59/04, 61/02</p>	<p>A1</p>	<p>(11) International Publication Number: WO 95/16734 (43) International Publication Date: 22 June 1995 (22.06.95)</p>
<p>(21) International Application Number: PCT/US93/12279 (22) International Filing Date: 16 December 1993 (16.12.93) (71) Applicant (for all designated States except US): E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): SHINOHARA, Kenichi [JP/JP]; 4-6-19, Eda-higashi, Midori-ku, Yokohama-shi, Kanagawa 223 (JP). NAKATANI, Mitsunobu [JP/JP]; Gurandohaitsu Izumigaoka 418, 2-1-15, Izumigaoka, Utsunomiya-shi, Tochigi 321 (JP). MATSUDA, Toyoharu [JP/JP]; 606 Izumi-cho, Izumi-ku, Yokohama-shi, Kana- gawa 245 (JP). (74) Agents: MALINOWSKI, Andrea, V. et al.; E.I. du Pont de Nemours and Company, Legal/Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).</p>		<p>(81) Designated States: US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published With international search report.</p>
<p>(54) Title: POLYACETAL RESIN COMPOSITION WITH REDUCED FORMALDEHYDE ODOR (57) Abstract A polyacetal resin composition having adhered to its surface a partial aliphatic acid ester of a polyhydric alcohol, said composition having reduced formaldehyde odor and resulting in molded articles having improved mold release and/or reduced formaldehyde odor.</p>		

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TITLE

POLYACETAL RESIN COMPOSITION
WITH REDUCED FORMALDEHYDE ODOR

BACKGROUND OF THE INVENTION

5 The present invention relates to a polyacetal resin composition having a substantially reduced formaldehyde odor. It further relates to a process for manufacturing a polyacetal resin molded article having a reduced formaldehyde odor and having improved mold release properties.

 Polyacetal resins, which have excellent combined properties in
10 tensile strength, stiffness, fatigue resistance, and chemical resistance, are extensively used. However, polyacetal resins can be deficient in that when held in a molten state at high temperatures for a long period of time during molding steps, such as injection molding, the resins can thermally degrade (thermal depolymerization), which cannot only result in the formation of a
15 pungent formaldehyde odor, but can also result in a gradual accumulation of formaldehyde in the resultant molded articles, which will diminish product characteristics.

 A number of stabilization remedies have been proposed in order to suppress formaldehyde gas generation from polyacetal resins. These
20 remedies, which may be effective for suppressing the degradation of polyacetal resins in the molten state and reducing the amount of formaldehyde gas which might be generated, are deficient in reducing the amount of formaldehyde gas which may be slowly generated while the molded article solidifies and cools. Therefore, such products may still have a
25 formaldehyde odor, which can be responsible for decreased working efficiency.

 Another possible remedy involved hydroxyl-group containing compounds. Compounds having hydroxyl groups in the molecule give the possibility of generating an unstable adduct with formaldehyde, even at
30 ambient temperature, so as to reduce the gaseous formaldehyde concentration. They include, for example, water and alcoholic compounds. However, these compounds, which are low boiling compounds, would readily evaporate and be lost even when mixed with an acetal resin. Alcohol compounds can be deficient in that they may absorb moisture and may
35 adversely affect the heat stability of the acetal resin.

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On the other hand, polyhydric alcohol compounds, after partial esterification with an aliphatic acid or the like, are solid, even at ambient temperature, and nonvolatile, presenting the possibility of using these materials by adding them to the resin. It is also known in the art that these compounds, which have lubricity, can also be used as mold release agents for acetal resins. However, when such a polyhydric alcohol fatty acid ester is mixed with an acetal resin to prepare resin pellets for molding, the ester tends to thermally degrade, thereby liberating the fatty acid portion, which in turn, can rather adversely affect the heat stability of the acetal resin. Such an ester may also completely react with formaldehyde at the initial mixing stage, so as to lose any effect for trapping formaldehyde in a final molded article. As such, there is currently no effect known to the present inventors available for reducing formaldehyde odor that may occur with acetal resin products.

Therefore, there is a demand for developing a technical means to reduce the formaldehyde odor of melt extruded polyacetal pellets and articles molded therefrom and also to reduce the amount of formaldehyde gas which may gradually be generated in the process during which the molded article solidifies and cools.

An extensive study by the present inventors has led to the finding that the above problems can be solved by adhering a partial aliphatic acid ester of a polyhydric alcohol to the surface of a polyacetal resin. As such, the present invention relates to a polyacetal resin composition, having reduced formaldehyde odor, comprising melt extruded polyacetal resin pellets whose surface has a partial aliphatic acid ester of a polyhydric alcohol adhered thereto. In addition, the present invention also relates to a process for manufacturing a molded polyacetal resin product having a reduced formaldehyde odor in the molded article and having improved mold release properties, comprising melt molding the polyacetal resin pellets whose surfaces have an aliphatic acid partial ester of a polyhydric alcohol adhered thereto.

DETAILED DESCRIPTION OF THE INVENTION

The polyacetal resins used in this invention are polyacetal resins which have been commonly known as such heretofore, including homopolymers or copolymers of formaldehyde, a formaldehyde cyclic oligomer, trioxane or tetraoxane; or of acetaldehyde, propionaldehyde, or the

like; or polymers obtained by copolymerizing such an aldehyde with a cyclic ether or cyclic acetal, such as ethylene oxide, propylene oxide, 1,3-dioxalene, or the like. The polyacetal resin is a linear polymer comprising $-(CH_2)_n-O-$ main chain units (n is a natural number) and/or $-(CHR-O)-$ units (R is an alkyl group), with terminal groups thereof being either not protected or being protected with a radical selected from the group consisting of $-O-CO-CH_3$, $-OCH_3$, and $-O(CH_2)_n-OH$, with the number average molecular weight being 10,000-100,000, preferably 20,000-70,000. Acetal resin compositions which are used in this invention may optionally be compounded, if needed, within the range of not adversely affecting the present invention, with heat stabilizers, antioxidants, plasticizers, lubricants, fillers, colorants, and the like.

The polyacetal resin is melt extruded to give polyacetal resin pellets. A partial aliphatic acid ester of a polyhydric alcohol compound is adhered to the surface of said pellets.

The term "partial fatty acid ester of a polyhydric alcohol compounds" as used in this invention means a polyhydric alcohol compound having at least one free hydroxyl group, with the remaining hydroxyl groups being esterified with higher aliphatic acids.

Polyhydric alcohols which are partially esterified with higher aliphatic acids include polyhydric alcohols having 2-10 carbon atoms, specifically, for example, ethylene glycol, diethylene glycol, propylene glycol, dipropylene glycol, glycerine, diglycerine, pentaerythritol, dipentaerythritol, trimethylol ethane, trimethylol propane, 1,2,4-butane triol, 1,2,6-hexane triol, various sugar alcohols and their intramolecular dehydration products; such as tetrityls, including threitol; pentitols including xylitol; hexitols, including mannitol, sorbitol; as well as an intermolecular dehydration product, sorbitan, and the like.

Higher aliphatic acids which may be used for partially esterifying these polyhydric alcohols include aliphatic acids containing 16-32 carbon atoms or mixtures thereof. They are specifically, for example, palmitic acid, stearic acid, behenic acid, lignoceric acid, cerotic acid, montanic, melissic acid, and the like.

The partial aliphatic acid esters of polyhydric alcohols are preferably solid at ambient temperature or work temperatures for ease of application to the acetal resin pellets. Particularly preferred are those

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having melting points in the range of 50-150°C, for example, for an application as a powder.

Partial aliphatic esters of these polyhydric alcohols can be prepared by a variety of reactions involving esterifying a polyhydric alcohol with no more than an equivalent amount of a higher aliphatic acid, hydrolysis of a completely esterified higher aliphatic acid ester of a polyhydric alcohol, an ester exchange reaction of a polyhydric alcohol with a higher aliphatic acid ester, and the like. The partial aliphatic acid esters of polyhydric alcohols which are actually on the market and are available commonly contain as byproducts the unreacted polyhydric alcohol or aliphatic acid. Accordingly, adding a large amount of these esters to the acetal resin pellets may adversely affect the thermal stability thereof because of the effect of an acid component present as a byproduct. Therefore, the partial aliphatic acid ester of a polyhydric alcohol preferably has an acid value of not higher than 2, particularly not higher than 1.

Partial aliphatic acid esters of polyhydric alcohols specifically include hydroxy ethylene stearate, hydroxy ethylene behenate, hydroxy ethylene montannate, glycerine monostearate, glycerine monobehenate, glycerine monomontannate, glycerine dibehenate, pentaerythritol monostearate, pentaerythritol monobehenate, pentaerythritol monomontannate, pentaerythritol distearate, pentaerythritol dibehenate, pentaerythritol dimontannate, sorbitol monostearate, sorbitol monobehenate, sorbitol distearate, sorbitan monostearate, sorbitan monobehenate, sorbitan monomontannate, sorbitan distearate, sorbitan dibehenate, sorbitan dimontannate, and the like.

A variety of means are available for adhering the partial aliphatic acid ester of a polyhydric alcohol to the surface of the melt extruded polyacetal resin pellets in this invention, depending upon the physical properties of the partial aliphatic acid ester of a polyhydric alcohol compound.

The above-mentioned partial aliphatic acid esters of polyhydric alcohols, which are high boiling materials, can be readily reduced into a powder form, and the powdery partial ester can be deposited onto the polyacetal resin pellets to accomplish adhering the ester to the polyacetal resin pellets. In this case, very small particles of a partial aliphatic acid ester

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of a polyhydric alcohol are physically adhered to the surface of the polyacetal resin pellets.

Another method of applying the partial aliphatic acid ester of a polyhydric alcohol to polyacetal resin pellets includes dissolving the aliphatic acid ester of a polyhydric alcohol in a suitable solvent, with the resultant solution being applied to polyacetal resin pellets, thereby covering the surface of the polyacetal resin pellets with the solution and vaporizing off the solvent. Solvents used in such a case include alcohols, such as methanol and ethanol, ketone solvents, such as acetone and methylethylketone, ester solvents, such as methyl acetate and ethyl acetate, and solvents, such as methyl cellosolve, ethyl cellosolve, butyl cellosolve, and the like.

Other methods may be used which include fluidizing a partial aliphatic acid ester of a polyhydric compound at high temperatures and bringing the fluidized powder into contact with pellets so as to fuse the partial aliphatic acid ester to the pellet surface.

Use in this invention of 0.01-5.0 parts by weight, preferably 0.02-1.5 parts by weight, of the above partial aliphatic acid ester of a polyhydric alcohol per 100 parts by weight of polyacetal resin is preferred for reduction of formaldehyde odors and improvement of mold release behavior of molded articles. Although it is also possible to use a partial aliphatic acid ester or a polyhydric alcohol in a ratio beyond the above range, normally a quantity within the above range is sufficient.

The present invention is now described specifically by the examples below.

EXAMPLES

The polyacetal resin used in the Examples below was a polyacetal homopolymer resin (a high productivity grade, DE8501NC10, equivalent to Delrin® 500 grade sold by E. I. du Pont de Nemours and Company, hereinafter Polyacetal Resin A). The partial aliphatic acid ester of a polyhydric alcohol used in the examples below was behenic acid monoglyceride (sold by Kao Company "Ekiseparl G-MB", hereinafter Compound B).

Example 1

100 parts by weight of a pelletized Polyacetal Resin A composition was warmed in an oven regulated at 80°C for 30 minutes, removed from the oven, and the heated pellets were sprinkled with 0.1 parts

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by weight of Compound B to generate a pellet material C having a film of Compound B on the surface thereof. The pellet material C was molded in a two-piece cap molding mold. Five caps were molded. The five caps were sealed in a 1 L polyethylene container immediately after molding. The container was kept at ambient temperature to allow monitoring formaldehyde concentration of the container at fixed time intervals. The formaldehyde concentration in the container was 18.6 ppm 12 hours later, 14.7 ppm 24 hours later, and 10.4 ppm one week later. The mold release pressure at which the molded product was extruded from the mold was measured by inserting a pressure gauge near a cap bottom plate. The mold release pressure was 72.2 kg/cm².

Comparative Example 1

Tests similar to Example 1 were carried out except for using untreated Polyacetal Resin A pellets. The formaldehyde concentration in the container was 32.2 ppm 12 hours later, 23.1 ppm 24 hours later, and 22.1 ppm one week later. The mold release pressure was 85.6 kg/cm². This example showed that a molded product from the polyacetal pellets having no addition of 0.1% behenic acid monoglyceride thereon had a formaldehyde concentration twice as high one week later compared to a molded product from polyacetal pellets having the addition, thereby indicating that the addition of behenic acid monoglyceride reduced the formaldehyde concentration level of said untreated pellets to one-half or less. The mold release pressure was higher when no behenic acid monoglyceride was used compared to said pressure in the case when the behenic acid monoglyceride was used, indicating that the addition of behenic acid monoglyceride onto the pellets improved mold release pressure.

Comparative Example 2

Tests similar to Example 1 were carried out except for adding 0.2% of behenic acid monoglyceride. The formaldehyde concentration in the container in this case was 27.1 ppm 12 hours later, 22.0 ppm 24 hours later, and 22.4 ppm one week later. The mold release pressure was 70.0 kg/cm². Although the mold release pressure was improved, as in the case of Example 1, the effect of reducing formaldehyde concentration was lost when such an amount was added to the pellets. This example showed that the behenic acid monoglyceride was actually not a pure single compound, but rather it contained, in addition to the monoglyceride, liberated behenic acid,

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or the like. Therefore, the suitable amount of addition of behenic acid monoglyceride is 0.05-0.15%, which also depends on the purity or the free acid component concentration of the corresponding monoglyceride.

Comparative Example 3

- 5 The composition used in Polyacetal Resin A was mixed with 0.1% of behenic acid monoglyceride and melt-mixed in a 35 mm twin screw extruder to prepare resin pellets D containing 0.1% of behenic acid monoglyceride. Resin pellets D were subjected to tests similar to those of Example 1. The formaldehyde concentration in the container was 45 ppm
10 12 hours later, and 24 hours later, as well as one week later. The mold release pressure was 81.6 kg/cm² with only a slight effect on mold release. Thus, adding the behenic acid monoglyceride to the polyacetal prior to extrusion caused a partial thermal degradation of the behenic acid monoglyceride, thereby liberating the acid component, which ended up
15 increasing the amount of formaldehyde generated. Thus, it is demonstrated that adding behenic acid monoglyceride to pellets is more effective for reducing the evolution of formaldehyde and/or for improving the mold release.

CLAIMS

1. A polyacetal resin composition whose surface has a partial aliphatic acid ester of a polyhydric alcohol adhered thereto.
2. The polyacetal resin composition of Claim 1 wherein the
5 amount of the partial aliphatic acid ester of a polyhydric alcohol used is 0.01-5.0 parts by weight per 100 parts by weight of the polyacetal.
3. The polyacetal resin composition of Claim 1 wherein the polyacetal is a homopolymer.
4. The polyacetal resin composition of Claim 1 wherein the
10 polyacetal is a copolymer.
5. A process for the manufacture of a molded polyacetal resin product having reduced formaldehyde odor or improved mold release after molding comprising the step of melt molding the polyacetal resin composition of Claim 1.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US93/12279

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) : C08K 3/20; C08J 5/00; C08L 59/02, 59/04, 61/02
US CL : 525/398, 400; 524/593

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 525/398, 400; 524/593

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 3,699,062 (STARR ET AL.) 17 OCTOBER 1972, ABSTRACT, Column 3, lines 29-75, Column 4, lines 1-75, Column 5, lines 1-56.	1-5
X	US, A, 4,649,179 (TAKAGAKI) 10 MARCH 1987, ABSTRACT, Column 1, lines 57-68, Column 2, lines 1-63, Column 3, lines 7-17.	1-5

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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Date of the actual completion of the international search

28 MARCH 1994

Date of mailing of the international search report

APR 25 1994

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